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(54) Title: EXTRUDED NANOCOMPOSITE MOULDED PART COMPRISING AT LEAST A POLYCONDENSATE AND A NANO-FILLER AND A PROCESS FOR ITS PRODUCTION

(57) Abstract: The invention relates to an extruded moulded part comprising at least a polycondensate with a melt strength such that the polycondensate is not suitable for extrusion applications per se and a nano-filler, and a process for its production. The major advantage of the extruded moulded part and the process according to the invention is that extruded moulded parts containing polycondensate grades with both high and low viscosities are available. It is for example possible to use polyamides and polyesters that have not been after-condensed in the extrude moulded part according to the invention. Preferably, the extruded moulded part according to the invention contains a polyamide with a relative viscosity of less than 4.3, determined in a 1 % solution of the polyamide in m-cresol at 25 °C. The invention also relates to a process for increasing the melt strength of a polycondensate composition that contains at least a polycondensate by adding an amount of nano-filler to the composition.

5 EXTRUDED NANOCOMPOSITE MOULDED PART COMPRISING AT LEAST
 A POLYCONDENSATE AND A NANO-FILLER AND A PROCESS FOR
 ITS PRODUCTION

10 The invention relates to an extruded moulded part comprising at least a polycondensate and a process for its production.

Such an extruded moulded part is commonly known, for example from Kunststoff Handbuch, Becker et al., Carl Hanser Verlag, München, 1990.

15 In the context of this application an 'extruded moulded part' is understood to be any object that can be obtained by means of extrusion, in particular a film, for example a flat film or a tubular film, a foam, a thin-walled object, for example a bottle, a tube or a hose, a thick-walled object, for 20 example a moulded profile, tube or plate, a fibre, a monofilament or a thread, for example cable insulation. 'Film' is understood to be a material with a thickness that is small in comparison with the length and/or width of the material, its maximum thickness being 25 about 250 micrometres. A 'thin-walled object' is understood to be an object at least part of which consists of a material with a thickness of more than about 250 micrometres and less than about 1 mm. A 'thick-walled object' is understood to be an object at 30 least part of which consists of a material with a thickness of more than about 1 mm.

'Extrusion' is understood to be a process in which a moulded part is formed from the melt and which comprises at least one step in which a cooling

melt is formed into a moulded part, for example a melt-drawing step.

The disadvantage of the extruded moulded part according to the state of the art is that the 5 polycondensate has a high melt viscosity (MV), in particular an MV that is higher than the MV of a polycondensate that forms part of moulded parts obtained with the aid of the injection-moulding technique. This greatly limits the choice of the 10 polycondensate to be used. It is commonly known to a person skilled in the art that, for the production of an extruded moulded part, the polycondensate composition from which the moulded part is produced must have a good melt processability. This is obtained 15 by choosing a polycondensate with a high MV, for example a polyamide with a relative viscosity (RV) of 4.0 or more, determined in a 1% solution of the polyamide in m-cresol at 25°C. The use of a polycondensate with a low MV for example leads to 20 fracture, for example during the production of films, or for example even to the impossibility of extruding films and thin-walled moulded parts.

The aim of the present invention is to provide an extruded moulded part comprising at least a 25 polycondensate with a melt processability such that the polycondensate is not suitable for extrusion applications per se, and a process for obtaining it.

The inventors have now surprisingly found that a moulded part can be extruded, which comprises at 30 least a polycondensate with a melt processability such that the polycondensate is not suitable for extrusion applications per se and a nano-filler. It has namely surprisingly been found that such a composition has

such a high melt strength that a moulded part can be extruded from said composition. Said composition is known per se, for example from EP-A2-605,005 ((Unitika), but not for extrusion applications.

5 From EP-A1-810,260 (BASF A.G.) is known a film containing polyamide 6 prepared from caprolactam in the presence of a finely dispersed fluoro-mica mineral. According to EP-A1-810,260, such a film has a low gas permeability, while other properties, such as
10 gloss, transparency and ductility, do not change appreciably relative to a film that does not contain the finely dispersed fluoro-mica mineral. The polyamide has a high RV of 4.3, determined in a 1% solution of the polyamide in m-cresol at 25°C.

15 The great advantage of the extruded moulded part according to the invention is that extruded moulded parts containing polycondensate grades with both high and low viscosities are now available. For example, polyamides and polyesters that have not been
20 after-condensed can be used in the extruded moulded part according to the invention.

Another advantage of the extruded moulded part according to the invention is that less energy is needed during the compounding of the nanocomposite
25 composition, and that the composition's thin processability is better. This leads to for example thinner films. Another advantage is that one grade of polycondensate can be used both for extrusion and for injection-moulding applications by adding or not adding
30 the nano-filler.

As an additional advantage the inventors found that the surface of the moulded parts according to the invention showed a greater gloss and

transparency, films according to the invention showed no contraction and the films according to the invention showed a lower gas permeability and the films could be produced with much greater blow-up ratios in film blowing.

More in general, the inventors have found that the addition of an amount of nano-filler to polycondensate leads to a drastic increase in the melt strength of the resulting composition. The invention hence also relates to a process for increasing the melt strength of a polycondensate composition that contains at least a polycondensate by adding an amount of nano-filler, preferably by adding 0.1 - 10 wt.% nano-filler, more preferably 0.2 - 7.5 wt.%, relative to the polycondensate.

Any polymer known to a person skilled in the art can be chosen as the polycondensate, in particular polyamide, polyester, polyether ester, polycarbonate, polyester amide and blends and copolymers thereof.

In particular, a polyamide or polyester is chosen.

Preferably the polycondensate according to the invention is a polyamide with a relative viscosity of less than 4.3, determined in a 1% solution of the polyamide in m-cresol at 25°C.

Any polymer with acid-amide bonds (-CONH-) between the repeating units can be chosen as the polyamide, more in particular polyamides and copolyamides obtained from ϵ -caprolactam, 6-aminocaproic acid, ω -enantholactam, 7-aminoheptanoic acid, 11-aminodecanoic acid, 9-aminononanoic acid, α -pyrrolidone and α -piperidone; polymers and copolymers

obtained in the polycondensation of diamines, for example hexamethylene diamine, nonamethylene diamine, undecamethylene diamine, dodecamethylene diamine and metaxylene diamine, with dicarboxylic acids, for example terephthalic acid, isophthalic acid, adipic acid and sebacic acid; blends of the aforementioned polymers and copolymers. Examples of such polymers are nylon 6, nylon 9, nylon 11, nylon 12, nylon 4,6 and nylon 6,6. Preferably nylon 6 is chosen.

10 In principle, all the usual polyesters and copolyesters are suitable for use as the polyester. Examples are polyalkylene terephthalates or copolyesters thereof with isophthalic acid, for example polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyalkylene naphthalates, for example polyethylene naphthalate (PEN), polypropylene naphthalate, polybutylene naphthalate (PBN), polyalkylene dibenzoates, for example polyethylene bibenzoate and copolyesters hereof. Preferably use is made of PET, PBT, PEN or PBN. Also suitable are block copolyesters which, in addition to hard polyester segments from the above group, contain thermoplastic polyesters, soft polyester segments derived from at least one polyether or aliphatic polyester. Examples of such block copolyesters with elastomeric properties are for example described in "Encyclopedia of Polymer Science and Engineering", Vol. 12, pp. 75 ff. (1988), John Wiley & Sons, and "Thermoplastic Elastomers", 2nd Ex., chapter 8 (1996), Hauser Verlag, and the references mentioned therein.

As the nano-filler, use can be made of any material known as such to a person skilled in the art. In particular, a 'nano-filler' is understood to be a

solid substance composed of anisotropic particles with a high aspect ratio, for example layered or fibrous inorganic materials.

A particle's aspect ratio is in the context 5 of this invention understood to be the ratio of an individual particle's largest and smallest dimension. More in particular, the aspect ratio of a plate is the ratio of the length and the average thickness of the plate, and the aspect ratio of a fibre is the ratio of 10 the length and the average diameter of the fibre. Preferably use is made of a solid substance composed of anisotropic particles with a high aspect ratio, said aspect ratio lying between 5 and 10,000, preferably between 10 and 10,000, more preferably between 100 and 15 10,000.

Suitable layered inorganic materials consist of plates with an average aspect ratio of between 5 and 10,000. The plates then have an average thickness of about 2.5 nm or less, and a maximum 20 thickness of 10 nm, preferably between about 0.4 nm and about 2.5 nm, more preferably between about 0.4 nm and about 2 nm. The average length of the plates is preferably from about 2 nm to 1,000 nm. Examples of suitable layered inorganic materials are 25 phyllosilicates, for example smectic clay minerals, vermiculite clay minerals and micas, and synthetic micas. Examples of suitable smectic clay minerals are montmorillonite, nontronite, beidellite, volkonskoite, hectorite, stevensite, pyroysite, saponite, sauconite, 30 magadiite, bentonite and kanyaite. Preferably montmorillonite is chosen.

The individual fibres in the suitable fibrous inorganic materials have an average aspect

ratio of 5 to 10,000. The diameter of the individual fibres is then about 10 nm or less, the maximum diameter being 20 nm, preferably between about 0.5 nm and about 10 nm, more preferably between about 0.5 nm
5 and about 5 nm. The average length of the individual fibres in suitable fibrous inorganic materials is usually about 2,000 nm or less, the maximum length being about 10,000 nm, preferably between about 20 nm and about 200 nm, more preferably between about 40 nm
10 and about 100 nm. Examples of suitable fibrous inorganic materials are imogolite and vanadium oxide.

The amount of nano-filler may be freely chosen; the amount will depend on for example the desired properties of the extruded moulded part to be
15 obtained and on e.g. the polycondensate chosen, the degree of delamination of the nano-filler and the degree of dispersion in the polycondensate. In the context of this application, 'nano-filler' is understood to be both the filler as commercially available in an aggregated form and the filler in a deaggregated and delaminated form, as is to be found in the extruded moulded part. The nano-filler has either not been pretreated or modified or it has been pretreated or modified, for example to promote
20 delamination. In the event of complete dispersion and delamination the amount of nano-filler is preferably 0.1 - 10 wt.%, relative to the polycondensate. Preferably the amount of nano-filler in polyamide is 0.1 - 10 wt.%, more preferably 0.2 - 7.5 wt.%, relative
25 to the polyamide. The minimum and maximum amounts can easily be determined by a person skilled in the art because no extruded moulded part can be obtained with

the composition with amounts below the minimum and above the maximum amounts.

The extruded moulded part according to the invention optionally comprises additives, for example 5 fillers and reinforcing materials, for example glass fibres and silicates, for example talcum, flame retardants, foaming agents, stabilisers, flow-promoting agents and pigments.

The extruded moulded part according to the 10 invention may consist of one or of several layers; in the latter case the other layers may consist of for example polyolefines, for example polyethylene or polyethylene copolymers, for example copolymers obtained from ethylene and (meth)acrylic acid or 15 barrier polymers, for example polyvinylidene chloride or copolymers obtained from ethylene and vinyl alcohol.

The invention also relates to a process for the production of the polycondensate nanocomposite moulded part by means of extrusion, characterised in 20 that the moulded part is extruded from a composition comprising at least a polycondensate with a melt processability such that the polycondensate is not suitable for extrusion applications per se and a nano-filler.

25 In particular, the known techniques can be used to produce the extruded moulded part according to the invention, for example extrusion, coextrusion, film blowing, profile extrusion, foam extrusion, blow-moulding, deep drawing, calendering and spinning. In 30 the case of film, the extrusion or coextrusion can be effected for example with the aid of the chill-roll technique or by means of film blowing.

The composition with which the extruded

moulded part according to the invention can be produced according to the invention can be obtained in various ways known to a person skilled in the art, for example by means of polymerisation of the monomers in the

5 presence of the nano-filler as published in EP-A2-605,005 or by melt-mixing the polycondensate and the nano-filler, for example with the aid of an extruder, for example using the process according to US-5,385,776 (AlliedSignal Inc.). To obtain the desired properties

10 it is important that good dispersion and delamination of the nano-filler take place in the polycondensate.

The extruded moulded part according to the invention can in particular be used for example in the form of a film as a packaging film, for example for

15 wrapping up foodstuffs, for example cheese and sausage.

The invention will now be elucidated with reference to examples without being limited hereto.

EXAMPLES

20

Examples I-VII and Comparative Examples A and B:

Polyamide flat films

Production of flat films

25 A series of flat films was produced using a Gottfert extruder (type 616) with the following properties: screw diameter 30 mm, length 20xD, film head width 150 mm, extruder temperature 250°C, chill roll temperature 110°C.

30

Polyamide

Akulon® K123: injection-moulding-grade polyamide 6, relative viscosity of 2.8 (DSM N.V., the Netherlands).

Akulon® F132E: film-grade polyamide 6, relative viscosity of 4.0 (DSM N.V., the Netherlands).

5

Nano-filler

Cloisite 20A (montmorillonite clay, Southern Clay Products, USA), consisting of 60 wt.% silicate and 40 wt.% organic matter (quaternary ammonium salt). The 10 quantities quoted in the tables relate to the silicate content.

The polyamide nanocomposite composition was prepared by melt-mixing the polyamide in an extruder with a polyamide nanocomposite masterbatch containing 15 80 wt.% nano-filler (silicate).

The results are summarised in Table 1. They show that it is not possible to produce a film using only a polyamide with a low viscosity, whereas a good 20 film can be produced with the composition according to the invention. All the viscosities in Table 1 and the following tables were determined in a 1% solution of polyamide in m-cresol at 25°C.

Table 1 : Polyamide flat films

Example	Poly- amide	Nano-filler (wt. %)	Processing parameters	Melt processability
A	K123	0	Q (rpm) 80 v (winding) (m/min) 20	no production possible; insufficient melt strength
I	K123	0.1	60 20	no production possible; insufficient melt strength
II	K123	0.2	60 20	good film
III	K123	1	60 20	good film
IV	K123	2.5	60 20	good film
V	K123	5	60 20	good film
VI	K123	7.5	60 20	inhomogeneous processing behaviour; poor film
VII	K123	10	60 30	no production possible; film could no longer be drawn
B	F132E	0	60 20	good film

Example VIII and Comparative Examples C and D:
polyamide tubular films

Production of the tubular films

5 A series of tubular films was produced using a Collin (type 130) with the following properties:
screw diameter 25 mm, length 20xD, standard universal screw; chill roll dimensions 126 x 600 mm; rubber roll dimensions 72 x 600 mm; maximum open loop path 25 mm.

10 Temperature 250°C; blow-up ratio: 3

Polyamide

Akulon® K123: injection-moulding-grade polyamide 6, relative viscosity of 2.8 (DSM N.V., the Netherlands).

15 Akulon® F136E: film-grade polyamide 6, relative viscosity of 4.3 (DSM N.V., the Netherlands).

Nano-filler

Cloisite 20A (montmorillonite clay, Southern Clay Products, USA), consisting of 60 wt.% silicate and 40 wt.% organic matter (quaternary ammonium salt). The quantities quoted in the tables relate to the silicate content.

The polyamide nanocomposite composition was prepared by melt-mixing the polyamide in an extruder with a polyamide nanocomposite masterbatch containing 80 wt.% nano-filler (silicate).

The results are summarised in Table 2. They show that the addition of a small amount of nano-filler to a polyamide with a low viscosity leads to an increase in the melt processability such that a good tubular film could be obtained.

Table 2: Polyamide tubular films

Example	Polyamide	Nano-filler (wt. %)	Film
C	K123	0	no production possible; insufficient viscosity
VIII	K123	5	good film; the film becomes increasingly transparent as the blow-up ratio increases (3-4-4.5)
D	F136E	0	good film

Examples IX-XI and Comparative Example E: Polyamide plate

Production

5 A series of plates was produced using a Schabenthalan with the following properties: head width 150 mm; smooth feed section; extrusion temperature 250°C; chill roll temperature 40°C; die width in head 1.9 mm; width of gap between rolls 1 mm; speed 50 rpm.

10

Polyamide

Akulon® F135C: extrusion-grade polyamide 6, relative viscosity of 4.1 (DSM N.V., the Netherlands).

15 **Nano-filler**

Cloisite 20A (montmorillonite clay, Southern Clay Products, USA), consisting of 60 wt.% silicate and 40 wt.% organic matter (quaternary ammonium salt). The quantities quoted in the tables relate to the silicate content.

20

The polycondensate nanocomposite composition was prepared by melt-mixing the polyamide in an extruder with a masterbatch containing Akulon® K123 + 5 wt.% nano-filler.

25

The results are summarised in Table 3. They show that the addition of a small amount of nano-filler to the polyamide led to an increase in the melt processability such as to prevent sagging of the plate.

30

Surprisingly, a better gloss and greater transparency were obtained, too. Sagging of plates during extrusion is a well-known phenomenon that occurs between the

- 15 -

injection-moulding die and the first roll. Sagging was prevented by increasing the melt processability.

Table 3: Polyamide plates

Example	Polyamide	Nano-filler (wt. %)	Plate
E	F135C	0	Sagging of the plate observed
IX	F135C	0.25	Less sagging
X	F135C	0.5	No sagging
XI	F135C	1	No sagging

CLAIMS

1. Extruded moulded part comprising at least a polycondensate with a melt strength such that the polycondensate is not suitable for extrusion applications per se and a nano-filler.
2. Extruded moulded part according to Claim 1, characterised in that the polycondensate is chosen from the group comprising polyamide, polyester, polyether ester, polycarbonate and polyester amide and blends and copolymers thereof.
3. Extruded moulded part according to Claim 2, characterised in that the polycondensate is chosen from the group comprising polyamide and polyester.
4. Extruded moulded part according to Claim 3, characterised in that the polycondensate is a polyamide with a relative viscosity of less than 4.3, determined in a 1% solution of the polyamide in m-cresol at 25°C.
5. Extruded moulded part according to any one of Claims 1-4, characterised in that the amount of nano-filler is 0.1 - 10 wt.%, relative to the polycondensate.
6. Extruded moulded part according to any one of Claims 1-5, characterised in that the amount of nano-filler is 0.2 - 7.5 wt.%, relative to the polycondensate.
- 30 7. Extruded moulded part according to any one of Claims 1-6, characterised in that the nano-filler is montmorillonite.

8. Extruded moulded part according to any one of Claims 1-7, characterised in that the moulded part is a film, a thin-walled object, a thick-walled object, a foam or a fibre.
- 5 9. Process for the production of a polycondensate nanocomposite moulded part by means of extrusion, characterised in that the moulded part is extruded from a composition comprising at least a polycondensate with a melt processability such that the polycondensate is not suitable for extrusion applications per se and a nano-filler.
- 10 10. Process for increasing the melt strength of a polycondensate composition comprising at least a polycondensate by adding an amount of nano-filler to the composition.
- 15 11. Process according to Claim 10, characterised in that 0.1 - 10 wt.% nano-filler is added.
12. Extruded moulded part and process as described and elucidated with reference to the examples.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C08K7/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 41060 A (SOLUTIA INC) 19 August 1999 (1999-08-19) page 15, line 24 – line 27 page 26 claims 1-41 ---	1-12
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer Siemens, T

INTERNATIONAL SEARCH REPORT

Int'l Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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